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Interim Protocol for the Automated Analysis of Semivolatile Organic Compounds by Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry

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INTERIM PROTOCOL FOR THE AUTOMATED ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED (GC/FT-IR) SPECTROMETRY

by

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The application of gas chromatography/Fourier transform infrared (GC/FT-IR) data to regulatory decisions requires the availability of validated analytical protocols. Such protocols are necessary for the generation of reliable analytical data. A GC/FT-IR protocol is described which is applicable to the determination of semivolatile organic compounds in wastewater, soils, sediments and solid wastes. The protocol is designed for the high-throughput automated analysis of multicomponent environmental and hazardous waste extracts. Wastewater analysis is based upon extracting 1 L of sample with methylene chloride and concentrating the extract to 1 mL. Solid waste analysis is based upon extracting 50 grams of sample and concentrating the sample extract to 1.0 mL. A gel permeation option is included to further purify those extracts which cannot be concentrated to the specified final volume. Using capillary GC/FT-IR techniques, wastewater identification limits of 150 to 400 ppb can be achieved with this method while the corresponding identification limits for solid samples are 3 to 8 ppm. Automated packed column GC/FT-IR identification limits are approximately a factor of five higher than the corresponding capillary GC/FT-IR values.

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ABSTRACT

The application of gas chromatography/Fourier transform infrared (GC/FT-IR) data to regulatory decisions requires the availability of validated analytical protocols. Such protocols are necessary for the generation of reliable analytical data. A GC/FT-IR protocol is described which is applicable to the determination of semivolatile organic compounds in wastewater, soils, sediments and solid wastes. The protocol is designed for the high-throughput automated analysis of multicomponent environmental and hazardous waste extracts. Wastewater analysis for semivolatile organic compounds is based upon extracting 1 L of sample with methylene chloride and concentrating the extract to 1 mL. The analysis of the semivolatile fraction derived from solid waste analysis is based upon extracting 50 grams of sample and concentrating the sample extract to 1.0 mL. A gel permeation option is included to further purify those extracts which cannot be concentrated to the specified final volume. Using capillary GC/FT-IR techniques, wastewater identification limits of 150 to 400 ppb can be achieved with this method while the corresponding identification limits for solid samples are 3 to 8 ppm. Automated packed column GC/FT-IR identification limits are approximately a factor of five higher than the corresponding capillary GC/FT-IR values. The most frequent obstacle to achieving these identification limits is expected to be the presence of large quantities of interfering high boiling co-extractants. These co-extractants would raise the identification limits by preventing the concentration of extracts to the desired final volume, thereby necessitating gel permeation cleanup, and/or by decreasing the spectral signal-to-noise of GC-volatile analytes by raising the spectral background intensity.

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ABBREVIATIONS AND SYMBOLS

A_D	-- Area of Detector Element
A/D	-- Analog/Digital
AOAC	-- The Association of Official Analytical Chemists
ASTM	-- American Society for Testing Materials
D*	-- Detector Specific Detectivity
EMSL-LV	-- The Environmental Systems Laboratory at Las Vegas
EPA	-- Environmental Protection Agency
FSCC	-- Fused Silica Capillary Column
FT-IR	-- Fourier Transform Infrared
GC	-- Gas Chromatography
GC/FT-IR	-- Gas Chromatography/Fourier Transform Infrared Spectrometry
GC/FT-IR/MS	-- Directly Linked Gas Chromatography/Fourier Transform Infrared/Mass Spectrometry
GC/MS	-- Gas Chromatography/Mass Spectrometry
GIFTS	-- Gas Infrared Fourier Transform Software
GM	-- Gram
GPC	-- Gel Permeation Chromatography
i.d.	-- inside diameter
IR	-- Infrared
IRC	-- Infrared Reconstructed Chromatogram
K-D	-- Kuderna-Danish
ppb	-- parts per billion
ppm	-- parts per million
L	-- Liter
MIQ	-- Minimum Identifiable Quantity
mL	-- Milliliter
mm	-- Millimeter
MS	-- Mass Spectral
N	-- Normal
NEP	-- Noise-Equivalent-Power
µL	-- Microliter
QA/QC	-- Quality Assurance/Quality Control
RRT	-- Relative Retention Time
S/N	-- Single-to-Noise-Ratio

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INTRODUCTION

The applicability of the gas chromatography/Fourier transform infrared (GC/FT-IR) spectrometric technique to the analysis of wastewater, soils, sediments, hazardous wastes, and diesel particulates has been demonstrated.[1-8] Although this technique is currently one to two orders of magnitude less sensitive than gas chromatography/mass spectrometry (GC/MS), with sufficient extract concentration, GC/FT-IR is capable of detecting about 75 percent of the GC/MS detectable analytes.[1] The implementation of recently proposed improvements in GC/FT-IR technology[9] promises to improve the sensitivity of this technique to near that of current GC/MS technology. The feasibility of the direct linked GC/FT-IR/MS method for multicomponent analysis promises an economical solution to GC/FT-IR confirmation and complementation of the GC/MS analytical method.[10-12] This economy will be realized through the availability of low cost FT-IR and MS detectors and through the development of powerful computer software to process the large quantities of spectral data generated by using two detectors for every analytical run.

But before the use of GC/FT-IR analysis for regulatory decisions becomes widely accepted by the academic, industrial, and governmental communities, validated protocols for its usage must be available. These protocols must be validated by procedures designated by the appropriate vehicles within the scientific community. The Association of Official Analytical Chemists (AOAC) and American Society for Testing Materials (ASTM) are such vehicles and both have proposed suitable validation procedures for analytical protocols.[13,14]

CONCLUSIONS AND RECOMMENDATIONS

The analytical protocol described herein is adequate for the identification of environmental contaminants at the mid ppb to low ppm range. The principal problem expected in applying this protocol to environmental samples is expected to be the concentration of solid waste extracts to 1 mL. In cases of this sort, the extract may be cleaned up by gel permeation or the analyst may settle for higher identification limits.

Computer software is required to determine real-time relative IR peak intensities. This is required to provide relative intensity, as well as frequency precision, acceptance criteria for analyte identification. In addition, a consensus is required from the spectroscopic community on suitable chemical candidates for vapor-phase frequency calibration of the GC/FT-IR system (one reviewer has suggested indene for this role). This consensus should be sought from the Coblentz Society and/or the appropriate ASTM committee.

Finally, the minimum identifiable quantities of typical environmental contaminants should be determined in a round-robin study. This study should employ laboratories equipped with different model GC/FT-IR systems. This study is necessary because there are currently 11 commercial suppliers of FT-IR spectrometers. The round-robin study should be coordinated through the appropriate ASTM and/or Coblentz Society Committees.

RESULTS AND DISCUSSION

The minimum identifiable quantity (MIQ) of 54 environmentally important compounds using on-line GC/FT-IR techniques are listed in Tables 1 and 2. The capillary GC/FT-IR MIQ's range from 300 ng of molecules with oxygen containing functional groups to 800 nanograms (ng) of the polynuclear aromatics fluorene and phenanthrene. This corresponds to a sample sensitivity of 150 to 400 parts per billion (ppb) for wastewater, if 1 L of water is extracted and the extract concentrated to 1 mL with 2 µL of extract analyzed. A 50 gram (gm) solid sample undergoing workup by the Appendix A method provides sample sensitivities ranging from 3 to 8 ppm. Note that all MIQ's listed in Tables 1 and 2 were determined using the same GC program. As a result the GC peak volumes (elution volumes) of every analyte were not optimized. For example, Gurka et al. report a factor of 4.5 difference in GC peak volumes between tetrachloroethylene and di-n-Butyl phthalate using the same GC program.[5] Although large GC/FT-IR peak volumes mean reduced sensitivity via analyte dilution, multicomponent analysis necessitates that the elution volume of each analyte cannot be optimized with a single GC run. This resulting sacrifice in sensitivity is made to ensure higher sample throughputs.

The minimum identifiable quantities listed in Tables 1 and 2 have been obtained with the Environmental Monitoring Systems Laboratory, Las Vegas, Nevada (EMSL-LV), GC/FT-IR system, which has been described elsewhere[1,4,5] and has recently been updated to include a Data General Nova 4 computer equipped with a high speed array processor and a Lark Model, Control Data 50 megabyte double disk drive. GC/FT-IR sensitivity values for strong infrared absorbers ranging between 200 ng for single beam and 50 ng for double beam systems have been reported by Griffiths.[15] However, dual-beam GC/FT-IR systems are not commercially available at this time. Recently, Taylor has reported identifiable FSCC/GC/FT-IR spectra for 40 ng of some compounds.[16] At this time the relative sensitivities of GC/FT-IR systems purchased from different manufacturers has not been assessed. However the MIQ's reported in this study have been generated under routine environmental analysis conditions and should be considered as realistically obtainable.

The parameters affecting GC/FT-IR sensitivity are listed in Table 3. These parameters break down into the broad classes of spectrometer, interface, chromatographic, computer, and molecular factors. In general, the analyst has control over only the chromatographic parameters and the lightpipe temperature. In some cases the analyst may have a choice of scan rates. A factor of three reduction in sensitivity has been reported on heating the lightpipe from ambient to 240°C[5] but Griffiths has concluded that this effect may be entirely eliminated by re-configuring the spectrometer collection optics.[9] An average factor of five improvement in sensitivity with the use of FSCC/GC-FT-IR has been reported.[1] This sensitivity gain is expected from smaller capillary

TABLE 1. FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED ON-LINE AUTOMATED IDENTIFICATION LIMITS FOR BASE-NEUTRAL EXTRACTABLES

No.	Compound	Identification Limit, µg	
		Packed[a] Column	Capillary[b] Column
	Isophorone	---	0.30
	Nitrobenzene	1.00	0.40
	Dimethyl phthalate	1.10	0.40
	Diphenyl ether	1.20	---
	2,4-Dinitrotoluene	2.00	0.30
	N-Nitroso-dimethylamine	2.00	0.30
	3-Methyl-2-butanone	2.00	---
	1,3-Dichlorobenzene	2.00	0.40
	Diethyl phthalate	2.00	0.40
	4-Chlorophenylphenyl ether	2.00	0.60
	Di-n-Butyl phthalate	2.10	0.80
	Di-n-Propyl phthalate	---	0.40
	Butyl benzyl phthalate	---	0.40
	2-Methylnapthalene	---	0.80
	1,4-Dichlorobenzene	3.00	0.30
	bis-2-Chloroethyl ether	3.00	1.00
	Hexachloroethane	3.00	0.40
	o-Nitrotoluene	3.30	---
	Aniline	3.30	0.40
	4-Chloroaniline	---	0.40
	2-Nitroaniline	---	0.40
	3-Nitroaniline	---	0.40
	4-Nitroaniline	---	0.55
	1,2,4-Trichlorobenzene	3.50	0.40
	n-Valeraldehyde	4.20	---
	Napthalene	5.00	0.40
	2-Chloronapthalene	5.00	0.80
	2,6-Dinitrotoluene	6.00	0.30
	bis-2-Chloro-isopropyl ether	6.00	0.40
	bis-2-Chloro-ethoxymethane	6.00	0.40
	4-Bromophenylphenyl ether	6.00	0.80
	N-Nitroso-di-propylamine	6.00	0.30
	N-Nitroso-di-phenylamine	6.00	0.80
	Thiophene	6.20	---
	1,2-Dichlorobenzene	7.00	0.50
	Acenapthene	7.00	---
	Acenapthylene	---	0.80
	1,3-Hexachlorobutadiene	7.50	0.80
	Fluorene	10.00	0.80

(continued)

TABLE 1. (Continued)

No.	Compound	Identification Limit, µg: Packed[a] Column	Identification Limit, µg: Capillary[b] Column
	Hexachlorocyclopentadiene	10.00	---
	Phenanthrene	---	0.80
	Benzyl alcohol	---	1.00

[a] Determined on-the-fly using on-column injection and with a 6 ft x 1/8 inch i.d. glass column packed with 1.5% OV-17 and 1.95% QF-1 on 80/100 mesh Gas Chrom Q. A helium flow of 30 mL/min was used and the GC was programmed from 70° to 225° at 10°/min. The interferometer scan rate was 0.3 cm/sec and 3 scans/2 sec were collected. The lightpipe was gold-coated with dimensions of 60 cm x 2.4 mm i.d. and was maintained at 240°C. A narrow band HgCdTe detector (3800-700cm^{-1}) with a 2 mm^2 focal chip was used.[5]

[b] Determined on-the-fly using splitless injection and a J & W DB-5 30 M x 0.32 mm fused silica capillary column (1.0 µm film thickness) at a helium flow of 1 mL/min and no makeup gas. The GC was programmed from 40° to 280°C at 10°/min. The interferometer scan rate was 1.2 cm/sec and 2 scans per second were collected onto magnetic disk. The lightpipe was gold-coated with dimensions of 12 cm x 1.5 (or 2.0) mm i.d. and was maintained at 280°C. A medium band HgCdTe detector [3800-700cm^{-1}; D*value (λpeak 1000 Hz, 1) > 1.0 x 10^{10}cm Hz$^{1/2}$W^{-1}] with a 1 mm^2 focal chip was used. These identification limits are a factor of 2.75 better than those reported in reference 1 and result from updating the system computer from 32K to 64K of mapped memory and collecting scans to disk rather than magnetic tape.

column, compared to packed column, elution volumes.[17] Clearly the relative sensitivities of GC/FT-IR systems, from different manufacturers, should be assessed via a round-robin study with standard solutions.

To establish acceptance criteria for analyte identification, the precision of real-time spectral frequencies were determined using the Digilab GC/S software. This software determines the nominal frequency in cm^{-1} at the peak top of the most intense IR bands within each spectrum. These frequency precisions are listed in Table 4 and for sharp IR peaks are ±1 cm^{-1} or less. Thus to report an analyte as "identified," the frequencies of the major IR bands in the analyte and library spectra should agree to at least ±1 cm^{-1} and the nominal spectral frequencies for the analyte and library spectra should be determined with the same computer software. Acceptance criteria for the relative intensities of the major IR bands in the analyte and library spectra should also be established, but at present the necessary computer software is not available.

TABLE 2. FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED ON-LINE AUTOMATED IDENTIFICATION LIMITS FOR ACIDIC EXTRACTABLES

No.	Compound	Identification Limit, μg[a]
1	Phenol	0.55
2	2-Chlorophenol	0.55
3	2-Cresol	0.55
4	4-Cresol	0.55
5	2-Nitrophenol	0.40
6	Benzoic acid	0.55
7	2,4-Dichlorophenol	0.55
8	4-Chlorophenol	0.95
9	2,4,6-Trichlorophenol	0.95
10	2,4,5-Trichlorophenol	0.95
11	2,4-Dinitrophenol	0.55
12	4,6-Dinitro-2-cresol	0.55

[a] Operating conditions are the same as those cited in footnote b of Table 1.

TABLE 3. GC/FT-IR SENSITIVITY PARAMETERS

Location	Nature	Effect
Spectrometer	Scan Rate	Spectral S/N (S/N α $\sqrt{\text{Nscans}}$)
	Source Output	Signal Intensity
	Computer	Data Treatment Capacity
	A/D Convertor	Data Transmission Capacity
Interface	GC/Column Type (packed or capillary)	Analyte Concentration
	Analyte Elution Volume	Analyte Concentration
	Lightpipe temperature	Spectral S/N (S/N $\frac{1}{\alpha}$ temperature)
	Detector D*	Intrinsic Detector Sensitivity
	Detector Element Area (A_D)	Signal Density at Detector (Noise-Equivalent-Power (NEP) = $\sqrt{A_D}/D^*$)
	Makeup Gas	Analyte Dilution
	Water Vapor	Reduces S/N
	Flow Rate	Analyte Concentration
Molecule	Structure	Intensity of Absorption
	Molecular Weight	Number of Molecules
	Boiling Point	Analyte Concentration

TABLE 4. REPRODUCIBILITY OF SOFTWARE-DETERMINED GC/FT-IR SPECTRAL FREQUENCIES

Compound	ν,CM-1a,b	No. Runs	No. Days	S.D.c
n-Nitroso-dimethylamine	2958.1	14	8	1.70
	1489.0	14	8	0.00
	1476.4	10	7	1.26
	1284.1	13	7	2.40
	1007.9	14	8	1.70
1,3-Dichlorobenzene	1577.4	13	7	1.50
	1454.9	13	7	2.08
	1078.0	10	7	2.11
	783.5	13	7	2.33
1,4-Dichlorobenzene	1476.6	14	7	1.09
	1092.0	14	7	0.00
	1013.5	13	7	1.92
	818.6	13	7	1.50
1,2-Dichlorobenzene	1458.0	13	7	0.00
	1126.3	11	7	2.72
	1036.7	12	7	3.55
	746.5	12	7	1.57
bis-2-Chloroethyl ether	2991.2	9	7	8.39
	1132.6	11	7	2.02
	1088.8	10	7	1.69
	755.3	6	6	3.01
n-Nitroso-di-propyl ether	2974.9	14	8	1.70
	2939.9	14	8	1.38
	2888.8	9	7	3.35
	1484.1	13	8	1.75
	1042.5	13	8	1.13
Nitrobenzene	1540.0	12	8	2.49
	1353.7	12	8	1.15
	852.5	4	4	5.20
Isophorone	2963.0	11	7	0.00
	2904.6	10	7	1.26
	2884.7	7	6	5.62
	1693.6	11	7	1.29
	1372.0	4	3	2.00

(continued)

TABLE 4. (Continued)

Compound	ν,CM-1a,b	No. Runs	No. Days	S.D.c
bis-2-Chloro-ethoxymethane	2959.0	6	6	3.58
	2892.6	7	7	5.53
	1159.8	10	8	1.93
	1119.6	7	7	4.28
	1033.6	11	8	2.16
Hexachlorobutadiene	1559.1	7	5	1.95
	982.7	9	7	2.00
	853.0	9	7	0.00
	798.9	9	7	1.76
2,6-Dinitrotoluene	1551.4	11	8	1.26
	1357.3	11	8	2.41
2,4-Dinitrotoluene	1605.0	10	8	0.00
	1548.0	13	8	3.00
	1350.0	12	8	0.00
Fluorene	3071.0	10	8	0.00
	1451.3	6	5	2.07
	737.0	8	6	0.00
Di-Phenylamine	1595.2	13	8	2.08
	1501.2	13	8	0.83
	1300.0	13	8	0.00
	745.4	7	7	1.13
Phenanthrene	3067.0	10	8	1.89
	805.6	10	7	1.26
	730.5	10	7	2.17

a Mean value for the indicated number of runs.
b Determined from the peak maximum using Digilab GC/S® software.
c Standard deviation for the indicated number of runs.

The wastewater[18] and solid sample[19-21] workup methods used in this protocol have been described in detail elsewhere. The wastewater workup is based on Method 625 and has been modified to allow the Fused Silica Capillary (FSCC) extract analysis method of Sauter and Betowski.[22,23] The solid sample workup technique has been developed by the Battelle, Midwest and Southern Institutes. This procedure has been validated for the largest solid sample size of any currently available method. A gel permeation option has been included for those extracts which cannot be sufficiently concentrated to attain the desired detection limit.

In addition to the earlier described frequency precisions, many other Quality Assurance/Quality Control (QA/QC) procedures are incorporated within the protocol. These include criteria for the instrumental centerburst intensity as a function of temperature and spectrometer day-to-day stability. QA/QC procedures are roughly divided into classes of Daily, Periodic, and Initial Setup checks. Daily QA/QC includes a 100 percent Line Test, Single Beam Test, Spectrometer and Mirror Align Tests, and Lightpipe and Beam Splitter protective procedures. Periodic QA/QC procedures include a detector check, frequency calibration, and capillary and packed column sensitivity tests. Initial setup QA/QC includes interferometer and detector checks, frequency calibration, an interface sensitivity check, the determination of minimum identifiable quantities of target compounds, and the preparation of a calibration plot of detector centerburst intensity versus lightpipe temperature.

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APPENDIX A-1

Interim Protocol for the Automated Analysis of Semivolatile Organic Compounds by Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry

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EMSL-LV, JULY 1984

INTERIM PROTOCOL FOR THE AUTOMATED ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED (GC/FT-IR) SPECTROMETRY

1.0 Scope and Application

1.1 This method covers the automated identification of solvent extractable semivolatile organic compounds, which are amenable to gas chromatography, by GC/FT-IR.

1.2 This method is applicable to the determination of extractable semivolatile organic compounds in wastewater, soils and sediments, and solid wastes. For example, benzidine can be subject to oxidation losses during solvent concentration; α-BHC δ-BHC, endosulfan I and II, and endrin are subject to decomposition under the alkaline conditions of the extraction step; and hexachlorocyclopentadiene and N-nitrosodiphenylamine decompose at higher temperatures. Other extraction and/or instrumentation procedures should be considered for unstable chemicals.

1.3 The identification limit of this method may depend strongly upon the level and type of gas chromatographicable (GC) volatile extractants. In addition, packed column GC/FT-IR identification limits are about a factor of five higher than the corresponding capillary column values. The values listed in Tables A-1 and A-2 represent the minimum quantities of semivolatile organic compounds which have been identified by the specified GC/FT-IR system, using this method and under routine environmental automated-analysis conditions. The corresponding minimum visually identifiable quantities are about a factor of two lower than the Table A-1 values. Capillary GC/FT-IR wastewater identification limits of 400 ppb may be achieved for weak infrared absorbers (polynuclear aromatics) with this method while the corresponding identification limits for solid samples are about 8 ppm. GC/FT-IR response factor studies indicate that the identification limits of the strongest infrared absorbers are at least a factor of 10 lower than the corresponding limits for weak infrared absorbers.

2.0 Summary of Method for GC/FT-IR Analysis

If this method is used to confirm gas chromatography/mass spectrometry (GC/MS) the GC/MS analyzed extract should be concentrated, at least 10-fold, using Kuderna-Danish (K-D) techniques, prior to

GC/FT-IR analysis. Otherwise, the following preparation techniques may be used.

2.1 Wastewater Analysis

A 1 to 2-liter sample of wastewater is extracted and worked up by EPA Method 625 (1). If fused silica capillary column GC/FT-IR analysis is employed the 625 base neutral (B/N) and acid extracts should be concentrated to 1-mL by K-D techniques. Just prior to analysis the two 1-mL extracts should be combined and concentrated to 1-mL by K-D. For packed column GC/FT-IR analysis, 1-mL B/N and acid extracts should be separately analyzed. At least two µL of extract should be injected into the gas chromatograph for both packed and capillary analyses.

2.2 Solid Waste Analysis

The isolation and cleanup procedures as originally developed for the analysis of municipal sludges for priority pollutants are the basis of this analysis (2-4). If fused silica capillary column GC/FT-IR analysis is employed the 625 base neutral (B/N) and acid extracts should be concentrated to 1-mL by K-D techniques. Subsequently, the two 1-mL extracts should be combined and concentrated to 1-mL by K-D. For packed column GC/FT-IR analysis, 1-mL B/N and acid extracts should be separately analyzed. At least two µL of extract should be injected into the gas chromatograph for both packed and capillary analyses.

2.3 A 50-g sample of chilled residual waste is extracted with methylene chloride using wet residual waste/solvent techniques aided by a high-speed homogenizer. Samples are extracted at pH 11 and again at pH 2 to extract base/neutral and acidic compounds, respectively.

3.0 Safety

3.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be minimized by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analysis.

3.2 All operations involving the use of methylene chloride, including the extraction of the waste sample, filtrations of the extract, and concentration of the extract, must be performed in a fume hood. Care should be taken to avoid skin contact with methylene chloride.

4.0 Interferences

4.1 Glassware and other sample processing hardware must be thoroughly cleaned to prevent contamination and misinterpretation. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents or purification of solvents by distillation in all-glass systems may be required.

4.2 Matrix interference will vary considerably from source to source, depending upon the diversity of the residual waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup to isolate the analytes of interest from interferences in order to achieve maximum sensitivity.

4.3 Clean all glassware as soon as possible after use by rinsing with the last solvent used. Glassware should be sealed/stored in a clean environment immediately after drying to prevent any accumulation of dust or other contaminants. See reference 5 for further guidelines on glassware cleaning.

5.0 Apparatus and Material

5.1 Extracting equipment.

5.1.1 ADT tissumizer (Tekmar SDT 182EN or equivalent).

5.1.2 Centrifuge (IEC CU-5000 or equivalent).

5.1.3 Screw-capped centrifuge bottles, 200 mL (Scientific Products C4144) with TFE-lined screw caps.

5.1.4 Fleakers® - 300 mL or equivalent.

5.1.5 Glass Syringe - 50 mL equipped with a 150 mm x 5 mm ID TFE tube.

5.2 Gel permeation chromatography cleanup.

5.2.1 Chromatography column - 500 mm x 19 mm ID (Scientific Products C-4670-106 or equivalent).

5.2.2 Bio-Beads SX-3, 200/400 mesh (Bio-Rad Laboratories 152-2750).

5.2.3 Glass wool.

5.2.4 Graduate cylinders - 100 mL.

5.2.5 GPC Autoprep (Analytical Biochemistry Labs, Inc., 1002 or equivalent with 25 mm ID column containing 50 to 60 g of Bio-Beads SX-3). (Optional)

5.3 Gas Chromatographic/Fourier Transform Infrared Spectrometric Equipment

5.3.1 Fourier Transform Infrared Spectrometer - A spectrometer capable of collecting at least one scan set per second at $8cm^{-1}$ resolution is required. A state-of-the-art A/D convertor is required since it has been shown that the throughput of single beam GC/FT-IR systems is A/D convertor limited (6).

5.3.2 GC/FT-IR Interface - The interface should be lightpipe volume-optimized for the selected chromatographic conditions (Lightpipe volume about 5 mL for packed columns; lightpipe volume 200-400 µL for capillary columns). The shortest possible inert transfer line (preferably fused silica) should be used to interface the end of the chromatographic column to the light-pipe. If fused silica capillary columns are employed, the end of the GC column can serve as the transfer line.

Griffiths has demonstrated that the optimum lightpipe volume is equal to the full width at half height of the GC eluate peak (see general reference number 5).

5.3.3 Packed Column 1 - For base/neutral compounds and pesticides a 6-foot glass column (1/4 in OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 Supelcoport (or equivalent).

5.3.4 Packed Column 2 - For acids, a 6-foot glass column (1/4 in OD x 2 mm ID) packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport (or equivalent).

5.3.5 Capillary Column - A fused silica DB-5 30 M x 0.32 mm capillary column with 1.0 µm film thickness (or equivalent).

5.3.6 Data Acquisition - A computer system dedicated to the GC/FT-IR system to allow the continuous acquisition, of scan sets for a full chromatographic run. Peripheral data storage systems should be available (magnetic tape and/or disk) for the storage of all acquired data. Software should be available to allow the acquisition and storage of every scan set, to locate the file numbers and transform high S/N scan sets, and to provide a real time reconstructed chromatogram.

5.3.7 Detector - A cryoscopic, medium-band HgCdTe (MCT) detector with the smallest practical focal area. Typical narrow-band MCT detectors operate from 3800-800 cm^{-1} but medium-band MCT detectors can reach 650 cm^{-1}. A 650 cm^{-1} cutoff (or lower) is desirable since it allows the detection of typical carbon-chlorine stretch and aromatic out-of-plane carbon-hydrogen vibrations of environmentally important organo-chlorine and polynuclear aromatic compounds. The MCT D* should be $\geq 1 \times 10^{10}$.

5.3.8 Lightpipe - Constructed of inert materials, gold coated, and volume-optimized for the desired chromatographic conditions (see GC/FT-IR Interface, Section 5.3.2).

5.3.9 Gas Chromatograph - The FT-IR spectrometer should be interfaced to a temperature programmable gas chromatograph equipped with a Grob-type (or equivalent) purged splitless injection system (7-9) suitable for capillary glass columns or an on-column injector system suitable for packed-glass columns. A short, inert, transfer line should interface the gas chromatograph to the FT-IR lightpipe and, if applicable to the GC detector. Fused silica GC columns may be directly interfaced to the light pipe inlet.

5.4.0 Dry Purge Gas - If the spectrometer is the purge-type, provisions should be made to provide a suitable continuous source of dry purge-gas to the FT-IR spectrometer.

6.0 Reagents

6.1 Sodium hydroxide - (ACS) 10 N in distilled water.

6.2 Hydrochloric acid - (ACS) concentrated, 12 N.

6.3 Sodium sulfate - (ACS) granular anydrous; conditioned at 400°C for 4 hours and rinsed with dry methylene chloride (20 mL/g).

6.4 Methylene chloride - Pesticide quality (Burdick and Jackson or equivalent).

6.5 Stock standards - Prepare stock standards from EPA Priority Pollutants Kit containing the pre-analyzed neat compounds (Chem Service or equivalent).

6.6 GPC calibration solutions:

a. Corn oil - 200 mg/mL in dichloromethane.

b. bis(2-ethylhexylphthalate) and pentachlorophenol - 4.0 mg/mL in dichloromethane.

7.0 Calibration Standards and Internal Standards

7.1 If quantitation is desired, prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will completely bracket the working range of the chromatographic system (two or more orders of magnitude are suggested).

7.2 If GC/FT-IR will not be used to confirm GC/MS results then prepare internal standard solutions. Suggested internal standards are 1-fluoronapthalene, anthracene, terphenyl, 2-chlorophenol, phenol, bis (2-chloroethoxy) methane, 2,4-dichlorophenol, phenanthrene,

anthracene, and butylbenzylphthalate. Determine the internal standard concentration levels from the minimum identifiable quantities (see Section 16.4).

8.0 Extraction of Solid Samples (Base/Neutrals)

8.1 The sample which should have been received and maintained at ice temperature is thoroughly mixed by homogenization in the sample bottle. Weigh a 50-g aliquot, or an appropriate weight as predetermined by screening analyses, into a 250 mL centrifuge tube.

8.2 Adjust the pH of the sample with 10 N sodium hydroxide to a pH of 11 or greater. Mix briefly with the homogenizer to ensure uniform sample pH.

8.3 Add 60 mL of methylene chloride to the sample tube and homogenize for 2 minutes at high speed. Rinse homogenizer off with a minimum quantity of reagent water, then with about 5-10 mL of methylene chloride. Additional amounts of methylene chloride may be added until total liquid level is near the top of the centrifuge tube. It may be necessary to extract abrasive samples using a sonication apparatus.

8.4 Centrifuge the samples at 1400 R.C.F. for 15 minutes. The mixture will separate into an aqueous layer over the methylene chloride extract. A solid cake or emulsion may form at the water-methylene chloride interface. If the emulsion interface between layers is more than one-half the size of the solvent layer, the analyst must employ a smaller sample to complete the phase separation. The optimum technique will depend upon the total solid content of the sample. Withdraw the organic extract from the centrifuge tube with a 50-mL glass syringe that has been equipped with a 150 mm x 5 mm ID TFE tube. Discharge the extract into a 300-mL fleaker®.

8.5 Add a second 60-mL volume of methylene chloride to the sample tube and complete the extraction procedure a second time. Combine the extracts in the fleaker®.

8.6 Perform a third extraction in the same manner, and then dry the combined extracts as stipulated in the Extract Drying Section.

9.0 Sample Extraction (Acids)

9.1 Adjust the pH of the sample, previously extracted for base/neutrals, with hydrochloric acid to a pH of 2 or less. The acid must be added slowly and with instant mixing to minimize foaming of the sample.

9.2 Extract the sample again using the procedures described in Sections 8.3 to 8.6. Discard the extracted residual water aliquots.

10.0 Extract Cleanup and Calibration (Optional)*

10.1 Place 20-25 g of Bio-Beads SX-3 into 200 mL beaker. Cover the beads with methylene chloride and allow the beads to swell overnight before packing the column. Put a glass wool plug in the bottom of a glass chromatographic column. Transfer the swelled beads to the column and continue to rinse the packed column with methylene chloride. Add to the top of the packed column a glass wool plug followed by a layer of glass beads which will prevent the Bio-Beads from floating to the top of the elution solvent. Wash the column with about 200 mL of methylene chloride. Just prior to exposure of the GPC packing, stop the elution by closing the stopcock on the chromatography column. Discard the eluate.

10.2 Transfer 5 mL of the GPC calibration solution (Section 6.6) to the Bio-Beads SX-3 column. Drain the column into a 100-mL graduated centrifuge tube until the liquid is just above the surface of the GPC packing. Wash the calibration solution onto the column with several 1-mL aliquots of methylene chloride. Next, elute the column with 200 mL of methylene chloride and collect 10-mL fractions. Analyze the fractions for bis-(2-ethylhexyl)phthalate and pentachlorophenol by GC/FID on a 1% SP-1240 DA column. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by gravimetric determination of the residue. Plot the concentration of each component in each fraction versus the total eluant volume. Discard the first fractions that elute up to a retention volume represented by ±85% recovery of the bis(2-ethylhexyl)phthalate. This corresponds to removal of most of the corn oil. Collect the fractions that elute up to a retention volume represented by 50 mL after the elution of pentachlorophenol. A typical procedure is to discard the first 60 mL, to collect the next 110 mL, and to wash the column with 250 mL of methylene chloride between samples.

10.3 Apply the above GPC separation procedure to an aliquot (1-4 mL) of the base/neutral or acid concentrate. The volume of concentrate submitted to GPC is determined by the amount of residue in the concentrate. Determine a residue weight of the concentrate by placing a 1-mL aliquot on tared aluminum foil pan, allowing the solvent to evaporate, and reweighing the pan. The volume of extract submitted to GPC should not exceed the capacity of the column or approximately 200 mg.

10.4 Collect the first 60 mL of eluant in a 100 mL graduate cylinder and pass the next 110 mL of eluant through a drying column containing anhydrous sodium sulfate and collect in a 500 mL K-D flask equipped

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* A test sample should be extracted as described above and tested as delineated in Section 10.3. If the residue weight is of the order of 1-5 mg the GPC workup may be disregarded. GPC cleanup is usually necessary if the sample extracts cannot be concentrated to the desired volume.

with a 10 mL concentrator tube. The drying column should be packed to a height of 60 mm with anhydrous sodium sulfate. Rinse the drying column with three 25-mL portions of methylene chloride.

11.0 GPC Cleaned Extract Concentration

11.1 Concentrate the GPC cleaned extract as described in Extract Concentration Procedure (Section 13.0).

11.2 Transfer the cleaned, concentrated extract to a 6-mL serum TFE capped bottle and store at 4°C for GC/FT-IR analysis.

12.0 Extract Drying

12.1 When the extract has not been subjected to a drying step (Na_2SO_4, prior to cleanup for example), the following extract drying procedure will be employed.

12.2 Pour the combined extracts, for each fraction resulting from the isolation procedure, through a drying column containing 3 to 4 inches of organics-free anhydrous sodium sulfate. The dried extract should be collected in a 500 mL K-D flask equipped with a 10-mL concentrator tube. The flask which originally contained the extract and the drying tube should be washed three times with 30-mL aliquots of the extraction solvent. These washes should be collected in a chilled K-D flask.

13.0 Extract Concentration

The dried extract will be concentrated as close as possible to 1-mL.

13.1 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the column by adding approximately 1 mL of the extracting solvent through the top to the column. Place the apparatus in a 60 to 65°C water bath with the concentrator tube partially immersed in the water and the lower rounded surface of the flask bathed with water vapor. Adjust the apparatus to complete concentration to approximately 10 mL in 15 minutes. At the proper rate of distillation, the balls of the column will chatter but the chambers will not flood. When the liquid has reached an approximate volume of 4 mL, remove the apparatus from the water bath and allow the solvent to drain for at least 10 minutes while cooling. Remove the Snyder column, and rinse the contents of the flask and its lower joint into the concentrator tube with 1 to 2 mL of the solvent employed in the extraction.

13.2 Remove the concentrator tube from the water bath, then fit with a micro-Snyder column. Organic-free nitrogen is employed to reduce the volume of the extract to approximately 1-mL. A Pasteur pipette is inserted into the top of the Snyder column to accomplish the final concentration. The concentrator tube and the pipette are washed with

approximately two 0.2-mL volumes of the extracting solvent. Dilute the final extract to 1 mL for GC/FT-IR analysis.

13.3 If the extract is to be stored before GC/FT-IR analysis, the extract can be transferred to an appropriately sized serum vial equipped with a Teflon-lined rubber septum and crimp cap. The extracts' volume should be scored on this vial, and appropriate sample identification consistent with the quality control and chain-of-custody requirements must be affixed to the vial. The extracts can then be stored in the dark at 4°C.

13.4 It is possible that samples which contain high concentrations of extractable organic compounds will not concentrate to 1.0 mL. For extracts of this type, the GPC Cleanup procedure may be used or the final volume after concentration should be adjusted to a minimal volume that affords an extract of suitable viscosity for micro syringe sampling.

14.0 Daily FT-IR Quality Assurance/Quality Control

14.1 One Hundred Percent Line Test - Set the GC/FT-IR operating conditions to those employed for the Sensitivity Test (see Section 14.2 or 14.3). Collect 16 scans over the entire detector spectral range. Plot the test and measure the peak-to-peak noise between 1800 and 2000 cm^{-1}. This noise should be $\leq$ 0.15%. Store this plot for future reference.

14.2 Single Beam Test - With the GC/FT-IR at analysis conditions, collect 16 scans in the single beam mode. Plot the co-added file and compare with a subsequent file acquired in the same fashion several minutes later. Note if the spectrometer is at purge equilibrium. Also check the plot for signs of deterioration of the light-pipe potassium bromide windows. Store this plot for future reference.

14.3 Align Test - With the light pipe and MCT detector at thermal equilibrium, check the intensity of the centerburst versus the signal-temperature calibration curve (see Section 16.6 and Figure 1). Signal intensity deviation from the predicted intensity may mean thermal equilibrium has not yet been achieved, loss of detector coolant, decrease in source output, or a loss in signal throughput resulting from lightpipe deterioration.

14.4 Mirror Alignment - Adjust the interferometer mirrors to attain the most intense align interferogram. Data collection should not be initiated until the align interferogram is stable. If necessary, align the mirrors prior to each GC/FT-IR run.

14.5 Lightpipe - The lightpipe and lightpipe windows should be protected from moisture and other corrosive substances at all times. For this purpose, maintain the lightpipe temperature above the maximum GC program temperature but below its thermal degradation limit. When not in use, maintain the lightpipe temperature slightly above ambient.

At all times maintain a flow of dry, inert, carrier gas through the lightpipe.

14.6 Beamsplitter - If the spectrometer is thermostated, maintain the beamsplitter at a temperature slightly above ambient at all times. If the spectrometer is not thermostated minimize exposure of the beamsplitter to atmospheric water vapor.

15.0 Periodic FT-IR Quality Assurance/Quality Control

15.1 With an oscilloscope, check the detector centerburst intensity versus the manufacturers specifications. Increase the source voltage, if necessary, to meet these specifications. For reference purposes, prepare a plot of time versus detector voltage over at least a 5-day period (see Figure 2).

15.2 Frequency Calibration - At the present time, no consensus exists within the spectroscopic community on a suitable frequency reference standard for vapor-phase FT-IR. One reviewer has suggested the use of indene as an on-the-fly standard. See reference 10 for other reference standards.

15.3 Capillary Column Interface Sensitivity Test - Install a 30 M x 0.32 mm fused silica capillary column coated with 1.0 µM of DB-5 (or equivalent). Set the lightpipe and transfer lines at 280°C, the injector at 225°C and the GC detector at 280°C (if used). Under splitless Grob-type injection conditions, inject 400 ng of nitrobenzene, dissolved in methylene chloride, while programming the GC from 40° to 280°C at 10°/min with a carrier gas flow of 1 mL/min. The nitrobenzene should be identified by the on-line library software search within the first five hits (nitrobenzene should be contained within the search library).

15.4 Packed Column Interface Sensitivity Test - Install a 6 ft x 1/8 inch glass column packed with 1.5% OV-17 and 1.95% QF-1 on 80/100 mesh Gas Chrom Q (or equivalent). Set the lightpipe at 240°C, transfer lines at 220°C, the injector at 225°C, and the GC detector at 280°C (if used). Inject on-column 1 microgram of nitrobenzene, dissolved in at least 2 µL of methylene chloride, while programming the GC from 70° to 220°C at 10°/min with a carrier gas flow at 30 mL/min. The nitrobenzene should be identified by the on-line library software search within the first five hits (nitrobenzene should be contained within the search library).

15.5 Checkup By Manufacturers' Servicemen - The spectrometer and interface should be checked by an authorized repairman for conformance to factory specifications.

16.0 Initial FT-IR Quality Assurance/Quality Control*

16.1 Interferometer - If the interferometer is air-driven, adjust the interferometer drive air pressure to manufacturers specifications.

16.2 MCT Detector Check - If necessary, install a new source and check the MCT centerburst with an oscilloscope versus the manufacturers specifications (if available). Allow at least five hours of new source operation before data acquisition.

16.3 Frequency Calibration - At the present time, no consensus exists within the spectroscopic community on a suitable frequency reference standard for vapor-phase FT-IR. One reviewer has suggested the use of indene as an on-the-fly standard. See reference 10 for other reference standards.

16.4 Minimum Identifiable Quantities - Using the GC/FT-IR operating parameters specified in Tables A-1 and A-2 (or equivalent) determine the minimum identifiable quantities for the compounds of interest.

16.5 Sensitivity Check - Determine the sensitivity of the GC/FT-IR interface (see Section 15.3 and 15.4).

16.6 Prepare a plot of lightpipe temperature versus MCT centerburst intensity (in volts or other vertical height units). This plot should span the temperature range between ambient and the lightpipe thermal limit in increments of about 20°C. Use this plot for daily QA/QC (see Section 14.3 and Figure 1).

17.0 GC/FT-IR Extract Analysis

17.1 Analysis - Analyze the dried methylene chloride extract using the chromatographic conditions specified in Table A-1 for packed or capillary column interfaces.

17.2 GC/MS Confirmation - Visually compare the analyte infrared (IR) spectrum versus the search library spectrum of the most promising on-line library search hits. Report, as identified, those analytes with IR frequencies for the five (maximum number) most intense IR bands ($S/N \geq 5$) which are within ± 1.0 cm^{-1} of the corresponding bands in the library spectrum. Choose IR bands which are sharp and well-resolved. If the analyte cannot be unequivocally identified, report its chemical functionality. See Table A-3 for nominal frequency precisions obtained for typical environmental contaminants using the EMSL-LV GC/FT-IR system with Digilab GC/S® software, and the operating conditions listed in footnote b of Table A-1. The software used to locate spectral peaks should employ the peak "center of gravity"

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* See Reference 11 for detailed criteria.

technique (12). In addition the IR frequencies of the analyte and library spectra should be determined with the same computer software.

17.3 GC/FT-IR Confirmation - After visual comparison of the analyte and library spectrum as described in Section 17.2 compare the relative retention times (RRT) of the analyte and an authentic standard of the most promising library search hit. The standard and analyte RRT should agree within ± 0.01 RRT units when both are determined at the same chromatographic conditions.

18.0 Quantitation

Although this protocol is primarily designed to aid GC/MS identification via confirmation, some quantitation guidelines are provided. Although liquid-phase IR quantitation is well-documented, little has been reported concerning on-line vapor-phase quantitation techniques (13).

18.1 Infrared Reconstructed Chromatogram (IRC) Technique - After analyte identification, construct a standard calibration curve of concentration versus infrared reconstructed chromatogram peak area spanning at least two orders of concentration magnitude. Choose the working range to bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.

18.2 Infrared Band Technique - After analyte identification construct a standard calibration curve of concentration versus infrared band intensity. For this purpose choose an intense, symmetrical and well-resolved IR band. The calibration curve should span at least two orders of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.

18.3 Supplemental GC Detector Technique - If a GC detector is used in tandem with the FT-IR detector, the following technique may be used; after analyte identification construct a standard calibration curve of concentration versus integrated peak area. The calibration curve should span at least two orders of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.

TABLE A-1. FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED ON-LINE AUTOMATED IDENTIFICATION LIMITS FOR BASE-NEUTRAL EXTRACTABLES

No.	Compound	Identification Limit, µg	
		Packed[a] Column	Capillary[b] Column
	Isophorone	---	0.30
	Nitrobenzene	1.00	0.40
	Dimethyl phthalate	1.10	0.40
	Diphenyl ether	1.20	---
	2,4-Dinitrotoluene	2.00	0.30
	N-Nitroso-dimethylamine	2.00	0.30
	3-Methyl-2-butanone	2.00	---
	1,3-Dichlorobenzene	2.00	0.40
	Diethyl phthalate	2.00	0.40
	4-Chlorophenylphenyl ether	2.00	0.60
	Di-n-Butyl phthalate	2.10	0.80
	Di-n-Propyl phthalate	---	0.400
	Butyl benzyl phthalate	---	0.400
	2-Methylnapthalene	---	0.800
	1,4-Dichlorobenzene	3.00	0.3
	bis-2-Chloroethyl ether	3.00	1.00
	Hexachloroethane	3.00	0.40
	o-Nitrotoluene	3.30	---
	Aniline	3.30	0.40
	4-Chloroaniline	---	0.40
	2-Nitroaniline	---	0.40
	3-Nitroaniline	---	0.40
	4-Nitroaniline	---	0.55
	1,2,4-Trichlorobenzene	3.50	0.40
	n-Valeraldehyde	4.20	---
	Napthalene	5.00	0.40
	2-Chloronapthalene	5.00	0.80
	2,6-Dinitrotoluene	6.00	0.30
	bis-2-Chloro-isopropyl ether	6.00	0.40
	bis-2-Chloro-ethoxymethane	6.00	0.40
	4-Bromophenylphenyl ether	6.00	0.80
	N-Nitroso-di-propylamine	6.00	0.30
	N-Nitroso-di-phenylamine	6.00	0.80
	Thiophene	6.20	---
	1,2-Dichlorobenzene	7.00	0.50
	Acenapthene	7.00	---
	Acenapthylene	---	0.80
	1,3-Hexachlorobutadiene	7.50	0.8C
	Fluorene	10.00	0.80

(continued)

TABLE A-1. (Continued)

No.	Compound	Identification Limit, µg: Packed[a] Column	Identification Limit, µg: Capillary[b] Column
	Hexachlorocyclopentadiene	10.00	---
	Phenanthrene	---	0.80
	Benzyl alcohol	---	1.00

[a] Determined on-the-fly using on-column injection and with a 6 ft x 1/8 inch i.d. glass column packed with 1.5% OV-17 and 1.95% QF-1 on 80/100 mesh Gas Chrom Q. A helium flow of 30 mL/min was used and the GC was programmed from 70° to 225° at 10°/min. The interferometer scan rate was 0.3 cm/sec and 3 scans/2 sec were collected. The lightpipe was gold-coated with dimensions of 60 cm x 2.4 mm i.d. and was maintained at 240°C. A narrow band HgCdTe detector (3800-700cm^{-1}) with a 2 mm^2 focal chip was used (14).

[b] Determined on-the-fly using splitless injection and a J & W DB-5 30 M x 0.32 mm fused silica capillary column (1.0 µm film thickness) at a helium flow of 1 mL/min and no makeup gas. The GC was programmed from 40° to 280°C at 10°/min. The interferometer scan rate was 1.2 cm/sec and 2 scans per second were collected onto magnetic disk. The lightpipe was gold-coated with dimensions of 12 cm x 1.5 (or 2.0) mm i.d. and was maintained at 280°C. A medium band HgCdTe detector [3800-700cm^{-1}; D*value (λpeak 1000 Hz, 1) > 1.0 x 10^{10}cm $Hz^{1/2}W^{-1}$] with a 1 mm^2 focal chip was used. These identification limits are a factor of 2.75 better than those reported in reference 15 and result from updating the system computer from 32K to 64K of mapped memory and collecting scans to disk rather than magnetic tape.

TABLE A-2. FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED ON-LINE AUTOMATED IDENTIFICATION LIMITS FOR ACIDIC EXTRACTABLES

No.	Compound	Identification Limit, µg[a]
1	Phenol	0.55
2	2-Chlorophenol	0.55
3	2-Cresol	0.55
4	4-Cresol	0.55
5	2-Nitrophenol	0.40
6	Benzoic acid	0.55
7	2,4-Dichlorophenol	0.55
8	4-Chlorophenol	0.95
9	2,4,6-Trichlorophenol	0.95
10	2,4,5-Trichlorophenol	0.95
11	2,4-Dinitrophenol	0.55
12	4,6-Dinitro-2-cresol	0.55

[a] Operating conditions are the same as those cited in footnote b of Table A-1.

TABLE A-3. REPRODUCIBILITY OF SOFTWARE-DETERMINED GC/FT-IR SPECTRAL FREQUENCIES

Compound	ν,CM-1a,b	No. Runs	No. Days	S.D.c
n-Nitroso-dimethylamine	2958.1	14	8	1.70
	1489.0	14	8	0.00
	1476.4	10	7	1.26
	1284.1	13	7	2.40
	1007.9	14	8	1.70
1,3-Dichlorobenzene	1577.4	13	7	1.50
	1454.9	13	7	2.08
	1078.0	10	7	2.11
	783.5	13	7	2.33
1,4-Dichlorobenzene	1476.6	14	7	1.09
	1092.0	14	7	0.00
	1013.5	13	7	1.92
	818.6	13	7	1.50
1,2-Dichlorobenzene	1458.0	13	7	0.00
	1126.3	11	7	2.72
	1036.7	12	7	3.55
	746.5	12	7	1.57
bis-2-Chloroethyl ether	2991.2	9	7	8.39
	1132.6	11	7	2.02
	1088.8	10	7	1.69
	755.3	6	6	3.01
n-Nitroso-di-propyl ether	2974.9	14	8	1.70
	2939.9	14	8	1.38
	2888.8	9	7	3.35
	1484.1	13	8	1.75
	1042.5	13	8	1.13
Nitrobenzene	1540.0	12	8	2.49
	1353.7	12	8	1.15
	852.5	4	4	5.20
Isophorone	2963.0	11	7	0.00
	2904.6	10	7	1.26
	2884.7	7	6	5.62
	1693.6	11	7	1.29
	1372.0	4	3	2.00

(continued)

TABLE A-3. (Continued)

Compound	ν,CM^{-1}[a,b]	No. Runs	No. Days	S.D.[c]
bis-2-Chloro-ethoxymethane	2959.0	6	6	3.58
	2892.6	7	7	5.53
	1159.8	10	8	1.93
	1119.6	7	7	4.28
	1033.6	11	8	2.16
Hexachlorobutadiene	1559.1	7	5	1.95
	982.7	9	7	2.00
	853.0	9	7	0.00
	798.9	9	7	1.76
2,6-Dinitrotoluene	1551.4	11	8	1.26
	1357.3	11	8	2.41
2,4-Dinitrotoluene	1605.0	10	8	0.00
	1548.0	13	8	3.00
	1350.0	12	8	0.00
Fluorene	3071.0	10	8	0.00
	1451.3	6	5	2.07
	737.0	8	6	0.00
Di-Phenylamine	1595.2	13	8	2.08
	1501.2	13	8	0.83
	1300.0	13	8	0.00
	745.4	7	7	1.13
Phenanthrene	3067.0	10	8	1.89
	805.6	10	7	1.26
	730.5	10	7	2.17

[a] Mean value for the indicated number of runs.
[b] Determined from the peak maximum using Digilab GC/S® software.
[c] Standard deviation for the indicated number of runs.

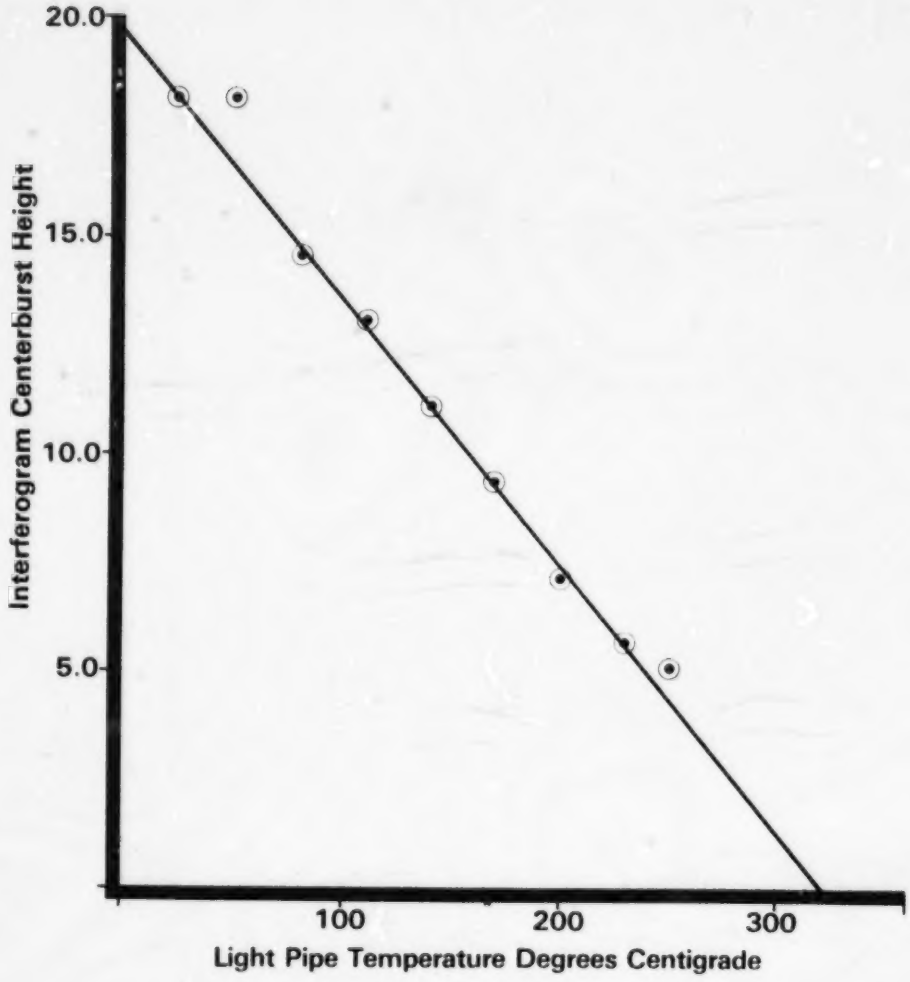

Figure 1. Lightpipe temperature effect on GC/FT-IR signal intensity (14).

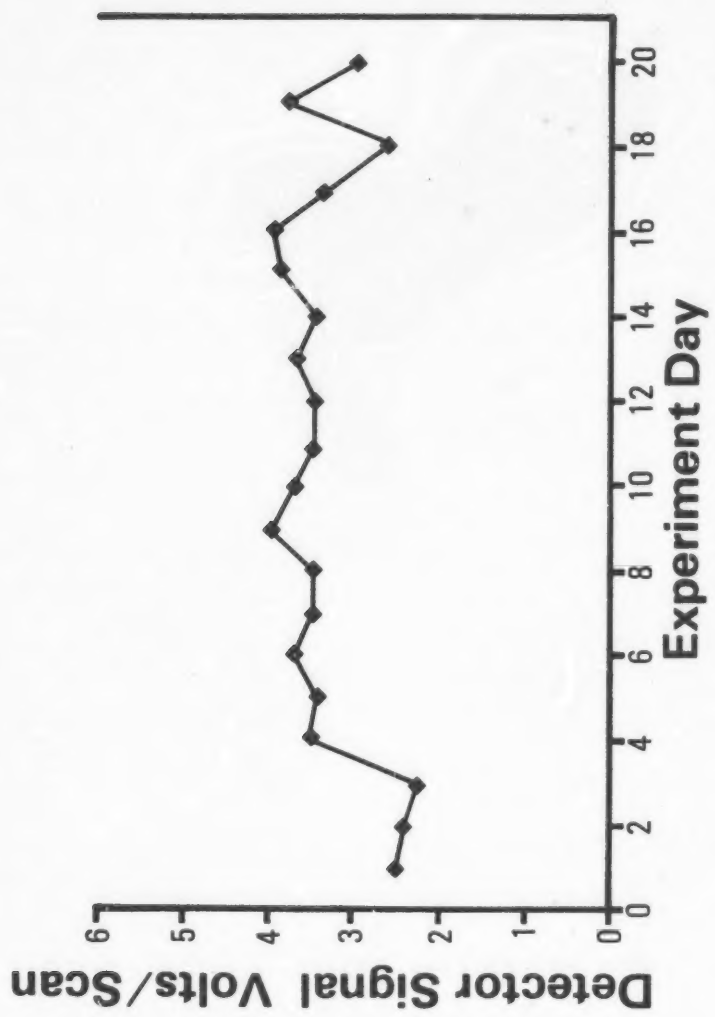

Figure 2. Detector signal variation with time (16).

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